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RED PHOSPHORUS

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Introduction

The clandestine synthesis of methamphetamine (meth) and other illegal drugs is a growing public health and environmental concern. For every pound of meth synthesized there are six or more pounds of hazardous materials or chemicals produced. These are often left on the premises, dumped down local septic systems, or illegally dumped in backyards, open spaces, in ditches along roadways or down municipal sewer systems. In addition to concerns for peace officer safety and health, there is increasing concern about potential health impacts on the public and on unknowing inhabitants, including children and the elderly, who subsequently occupy dwellings where illegal drug labs have been located.

The Office of Environmental Health Hazard Assessment (OEHHA), in cooperation with the Department of Toxic Substances Control (DTSC), has been charged with assisting in identifying and characterizing chemicals used or produced in the illegal manufacturing of methamphetamine, which pose the greatest potential human health concerns. To address in part this growing environmental problem and the need for public health and safety professionals to make appropriate risk management decisions for the remediation of former methamphetamine laboratory sites, OEHHA has developed two types of chemical-specific information documents.

The first set, technical support documents (TSDs), are referenced, multi-page publications, which contain important health and safety data, exposure limits, and key information for recognizing chemicals used or produced during the manufacturing of methamphetamine. These documents will likely be most helpful to health and safety officers, industrial hygienists, or others interested in more detailed toxicological information. The second set, two-page fact sheets, contain much of the same information as the corresponding TSDs; however, the details are presented in a more succinct, graphical format. The fact sheets will be helpful to individuals, including the public, who want to be able to quickly recognize potential chemicals of concern found in illegal methamphetamine labs in order to avoid inadvertent exposures and resulting health impacts.

For more information or to obtain copies of these and other documents, contact:

DEPARTMENT OF TOXIC SUBSTANCES CONTROL

P.O. Box 806 Sacramento, CA 95812-0806

www.dtsc.ca.gov/SiteCleanup/

OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT

P.O. Box 4010 Sacramento, CA 95812-4010

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I. Chemical Name

A. RED PHOSPHORUS (Pn)

B. Synonyms

Red amorphous phosphorus, violet phosphorus (Hazardtext, 2003).

II. Role in Clandestine Drug Synthesis: Methamphetamine

Red phosphorus is combined with elemental iodine to produce hydriodic acid (HI), which is used to reduce ephedrine or pseudoephedrine to methamphetamine.

III. Chemical Description

A. Appearance

Opaque, amorphous, or crystalline; orange-red, dark red, violet/dark red-purple, reddish brown; granular, pill, or powder (Turkington, 2000; Corbridge, 1995; Van Wazer, 1958; Acros, 2000).

B. Taste

Not available.

C. Odor

None (Turkington, 2000).

D. Odor Threshold

Not applicable.

E. Irritancy Threshold

Not available.

F. Odor Safety Class

Not applicable.

G. Vapor Density

The vapor density of red phosphorus is 4.77 (air = 1); therefore, red phosphorus is heavier than air (Aldrich, 2001).

H. Vapor Pressure

0.03 mmHg at 21° C (70° F) (Aldrich, 2001).

IV. Containers and Packaging

A. Commercial Products

Red phosphorus is a component of matchbook strike plates and is used as an ingredient in certain commercial rat and cockroach poisons (Turkington, 2000). Red phosphorus is used in the manufacture of pyrotechnics, safety matches, semiconductors, fertilizers, pesticides, incendiary

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shells, smoke bombs, and tracer bullets (HSDB, 2001). It is also used in organic synthesis reactions and in the manufacture of phosphoric acid, phosphine, phosphoric anhydride, phosphorus pentachloride, and phosphorus trichloride (HSDB, 2001). Red phosphorus is also used in electroluminescent coatings and in flame retardants for polymers (HSDB, 2001; NJDH, 2003).

B. Pharmaceutical Use

No pharmaceutical uses for red phosphorus were identified.

V. Chemical Hazards

A. Reactivity

Although it is stable at normal temperature and pressure, red phosphorus is a flammable solid and may pose a moderate explosion hazard by chemical reaction or on contact with organic materials (Acros, 2000; Turkington, 2000; Lewis, 2002). At normal temperature and humidity, red phosphorus reacts slowly with water vapor and oxygen in the air to form phosphine gas, which is extremely toxic, and a mixture of phosphorus oxyacids. This reaction can be accelerated by higher temperatures or trace concentrations of metals, including reducing metals that are used in plumbing pipes and fittings (e.g., iron and zinc) (Van Wazer, 1958). Certain products of anaerobic bacterial metabolism (e.g., hydrogen sulfide) can also reduce phosphorus to phosphine. These metals and reducing chemicals may be present in sink traps and sewer pipes.

Red phosphorous reacts with oxidizing agents, reducing agents, peroxides, strong alkalis (e.g., sodium hydroxide or potassium hydroxide), halogens, halides, and organic matter (YunPhos, 2002). If it comes into contact with oxidants (e.g., chlorine, fluorine, or bromine), red phosphorous may burn spontaneously or explode. Red phosphorous reacts vigorously with cesium, lithium, potassium, rubidium, sodium, and sulfur and explodes when combined with ammonium nitrate and moist chlorates (Hazardtext, 2003). Red phosphorous sublimes (transitions from a solid to a vapor) at 416° C (781° F) (Acros, 2000). The vapor is highly toxic and unstable, undergoing violent exothermic oxidation when it comes into contact with oxygen, chlorine, or other oxidants.

B. Flammability

Red phosphorous is a flammable solid and is readily combustible. It will not ignite spontaneously but may be ignited by an ignition source, heat, friction, static electrical spark, oxidizing agents, or physical impact (Acros, 2000; YunPhos, 2002; HCI, 1996; Hazardtext, 2003). Red phosphorous may re-ignite even after fire is extinguished (Acros, 2000). The auto ignition temperature for red phosphorous is 260° C (500° F). At high temperatures and in the absence of air, red phosphorous can burn, producing white phosphorous (Turkington, 2000; Hazardtext, 2003). Vapors may be heavier than air and can spread along the ground and collect in low or confined areas (Acros, 2000).

Hazardous decomposition products of red phosphorus combustion include phosphine, phosphorous oxides, white phosphorous, and phosphoric acid (Acros, 2000; Mallinckrodt, 2001). When red phosphorus is burned, phosphorus pentoxide is produced (Turkington, 2000). Phosphorous pentoxide absorbs water vapor from the air, producing corrosive phosphoric acid (HCI, 1996). Red phosphorous may explode if mixed with chemical oxidants (NJDH, 2003). Containers of red phosphorus may explode in the heat of a fire (Acros, 2000). In the presence of an ignition source, airborne red phosphorous dust may explode (Aldrich, 2001; Corbridge, 1995).

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C. Chemical Incompatibilities

Red phosphorus reacts explosively with a large number of compounds and elements (Acros, 2000). Red phosphorous forms sensitive explosive mixtures with metal halogenates (e.g., chlorates, bromates, or iodates of barium, calcium, magnesium, potassium, sodium, or zinc), ammonium nitrate, mercury(I) nitrate, silver nitrate, sodium nitrate, and potassium permanganate (Lewis, 2002).

If mixed with alkalis (e.g., sodium or potassium hydroxide) and heated, red phosphorus may react violently or ignite. Violent reaction or ignition may also occur if red phosphorus is combined with fluorine, chlorine, or liquid bromine. Red phosphorous reacts with hot alkalis or hydriodic acid to form phosphine gas, which may ignite (Lewis, 2002). Red phosphorous also reacts with halogens, halides, sulfur, oxidizing materials, oxygen, alkaline hydroxides, bases, peroxides, and perchlorates (Acros, 2000; Aldrich, 2001; HCI, 1996; NJDH, 2003).

Red phosphorus is incompatible with metals (aluminum and magnesium powders, beryllium, copper, copper containing alloys, and manganese (HCI, 1996; Aldrich, 2001; Lewis, 2002)), metal oxides (copper oxide, manganese dioxide, lead oxide, mercury(II) oxide, silver oxide, and chromium trioxide), metal peroxides (lead peroxide, potassium peroxide, and sodium peroxide), and metal sulfates (barium sulfate and calcium sulfate). Red phosphorus is also incompatible with nitric acid (Lewis, 2002).

Conditions to Avoid: Avoid light, ignition sources, dust generation, excess heat, oxidizers, flammable materials, friction, and physical impact (Acros, 2000; Mallinckrodt, 2001; Central, 1994; Lewis, 2002). Under wet alkaline conditions, red phosphorus slowly releases phosphine gas, which is highly toxic and highly flammable (HCI, 1996).

VI. Health Hazards

A. General

Red phosphorus, *in pure form*, does not usually represent a significant health hazard; it is essentially non-volatile, insoluble in water, and poorly absorbed (Mallinckrodt, 2001; HSDB, 2001). However, red phosphorus may be contaminated with white phosphorus, and symptoms such as nausea, vomiting, abdominal pain, or garlic odor indicate poisoning by the latter (Mallinckrodt, 2001). Therefore, exposure to contaminated red phosphorus may result in adverse effects on health, including irritation of the skin, eyes, lungs, and gastrointestinal tract (HSDB, 2001; Central, 1994; Dastech, 2001).

The acute, chronic and route-specific symptoms described below are based in part on the assumption that the source of exposure is red phosphorus contaminated with white phosphorus. Additionally, red phosphorus can react with chemicals commonly found in the environment (see additional information in section VI, A above), and the products of these reactions may present a significant health hazard.

B. Acute Effects

Red phosphorus may be harmful if absorbed through skin, ingested, or inhaled, and may cause irritation of the skin, eyes, upper respiratory tract, gastrointestinal tract, and mucous membranes (Aldrich, 2001; Central, 1994). Inhalation of red phosphorus dust may cause bronchitis (Central, 1994). Ingestion of red phosphorus may also cause stomach pains, vomiting, and diarrhea

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(Aldrich, 2001). Effects may vary from mild irritation to severe destruction of tissue depending on the intensity and duration of exposure (Aldrich, 2001; Dastech, 2001).

C. Chronic Effects

Prolonged and/or repeated skin contact may result in dermatitis (Acros, 2000). Chronic exposure may cause kidney and liver damage, anemia, stomach pains, vomiting, diarrhea, blood disorders, and cardiovascular effects (Acros, 2000; Central, 1994; Dastech, 2001; Mallinckrodt, 2001). Chronic ingestion or inhalation may induce systemic phosphorus poisoning. If red phosphorus is contaminated with white phosphorus, chronic ingestion may cause necrosis of the jaw bone ("phossy-jaw") (Mallinckrodt, 2001).

D. Skin Contact

Prolonged and/or repeated contact to red phosphorus may cause irritation and/or dermatitis (Acros, 2000). If red phosphorus is contaminated with white phosphorus, contact may cause deep, slow healing burns (Mallinckrodt, 2001). Red amorphous phosphorous may cause thermal burns (HCI, 1996).

E. Eye Contact

Red phosphorus may cause eye irritation and may result in corneal injury (Acros, 2000). If red phosphorus is contaminated with white phosphorus, eye contact can cause severe irritation and burns (Mallinckrodt, 2001).

F. Inhalation

Red phosphorus may cause respiratory tract irritation upon inhalation (Acros, 2000). It is not considered highly toxic; however, acute exposure may cause coughing, bronchitis, and possible liver or kidney impairment if contaminated with white phosphorus (Mallinckrodt, 2001).

G. Ingestion

Red phosphorus is not readily absorbed and, in pure form, is considered non-poisonous. However, if it is contaminated with white phosphorus, it may cause liver and kidney damage, irritation of the digestive tract, and may be fatal if swallowed (Acros, 2000; Mallinckrodt, 2001). If red phosphorus is ingested, possible contamination with white phosphorus must be considered; symptoms indicative of this are nausea, vomiting, abdominal pain, or a garlic odor on the breath (Mallinckrodt, 2001).

H. Predisposing Conditions

Individuals with pre-existing skin disorders, eye problems, jaw or tooth abnormalities, or impaired liver, kidney or respiratory function may be more susceptible to the effects of red phosphorus (Mallinckrodt, 2001).

I. Special Concerns for Children

No information found.

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VII. First Aid

A. Eyes

Immediately flush eyes with copious amounts of water for at least fifteen minutes, occasionally lifting upper and lower eyelids. Get medical attention immediately (Acros, 2000).

B. Skin

Remove contaminated clothing and shoes. Wash skin with soap and water for at least fifteen minutes. Seek medical attention (Acros, 2000).

C. Ingestion

Do not induce vomiting, but give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention immediately (Mallinckrodt, 2001). When medical attention is sought, make it clear that the individual was exposed to red amorphous phosphorous, and that potential contamination with white phosphorous is a concern (HCI, 1996).

D. Inhalation

Remove individual to fresh air immediately. If person is not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention (Acros, 2000).

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VIII. Standards for Inhalation Exposure

A. Occupational Exposure Limits (NIOSH, 1997; ACGIH, 1994)

1. Ceiling Limit (C) (not to be exceeded at any time):

Not established.

2. Short-Term Exposure Limit (STEL or ST): Not established.

3. 8-Hour Time Weighted Average (TWA): Not established.

4. 10-Hour Time Weighted Average (TWA): Not established.

Immediately Dangerous to Life & Health (IDLH): Not established.

Important Definitions Follow:

Ceiling Limit (C) is a concentration that must not be exceeded during any part of the workday.

<u>Short-Term Exposure Limit (STEL or ST)</u> is a 15-minute time-weighted average concentration that should not be exceeded during any part of the workday.

8-Hour Time Weighted Average (8-hour TWA) concentration is an exposure standard that must not be exceeded during any 8-hour work shift of a 40-hour workweek. 8-Hour TWA exposure standards established by the Occupational Safety and Health Administration (OSHA) are called Permissible Exposure Limits (PELs). 8-Hour TWA exposure standards established by the American Conference of Governmental Industrial Hygienists (ACGIH) are called Threshold Limit Values (TLVs).

<u>10-Hour Time Weighted Average</u> (10-hour TWA) concentration is an exposure standard that must not be exceeded during a 10-hour workday of a 40-hour workweek. 10-Hour TWA exposure standards developed by the National Institute for Occupational Safety and Health (NIOSH) are called <u>Recommended Exposure Limits</u> (RELs).

Immediately Dangerous to Life & Health (IDLH) defines a concentration which poses a threat of death or immediate or delayed permanent health effects, or is likely to prevent escape from such an environment in the event of failure of respiratory protection equipment. IDLH values are developed by the National Institute for Occupational Safety and Health (NIOSH).

"Skin" notation (NIOSH): significant uptake may occur as a result of skin contact. Therefore, appropriate personal protective clothing should be worn to prevent dermal exposure.

B. Emergency Response Planning Guidelines (1 hour or less) (AIHA, 2002)

ERPG-1 (protective against mild, transient effects): Not established.

2. ERPG-2 (protective against serious adverse effects): Not established.

ERPG-3 (protective against life-threatening effects): Not established.

Emergency Response Planning Guidelines (ERPGs) are developed by the American Industrial Hygiene Association (AIHA) to assist in planning and preparation for catastrophic accidental chemical releases. ERPGs allow emergency response planners to estimate the consequences of

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large-scale chemical releases on human health, and evaluate the effectiveness of prevention strategies and response capabilities. ERPGs assume that the duration of exposure is one hour or less. They are not intended to be used as limits for routine operations and are not legally enforceable.

Definitions for the three ERPG levels are:

- ERPG-1: an estimate of the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.
- ERPG-2: an estimate of the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
- <u>ERPG-3</u>: an estimate of the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

C. Acute Reference Exposure Level (1-hour exposure) (OEHHA, 1999)

Level protective against mild adverse effects:

Not established.

D. Chronic Reference Exposure Level (multiple years) (OEHHA, 2002)

Level protective of adverse health effects:

Not established.

Reference Exposure Levels (RELs) are developed by the California EPA's Office of Environmental Health Hazard Assessment (OEHHA). A REL is a concentration at or below which no adverse health effects are anticipated, even in the most sensitive members of the general population (for example, persons with pre-existing respiratory disease). RELs incorporate uncertainty factors to account for information gaps and uncertainties in the toxicological data. Therefore, exceeding a REL does not necessarily indicate an adverse health impact will occur in an exposed population. Acute RELs are based on an assumption that the duration of exposure is one hour or less. Chronic RELs are intended to be protective for individuals exposed continuously over at least a significant fraction of a lifetime (defined as 12 years).

E. Chronic Reference Concentration (lifetime exposure) (IRIS, 2003)

Level protective of adverse health effects:

Not established.

IX. Environmental Contamination Concerns

A. Surface Water

Red phosphorus will slowly degrade by disproportionating and hydrolysis to phosphine (PH₃) and phosphorus acids in the environment. Phosphine is very reactive and usually undergoes rapid oxidation. The final products, phosphates, are harmless. In wastewater, red phosphorus will adsorb to sewage sludge. Red phosphorus is harmful to aquatic organisms (EFRA, 2001).

B. Groundwater

No information available.

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C. Drinking Water

No information available.

Suggested No Adverse Response Level (NAS, 1980):

Not established.

Preliminary Remediation Goal for Tap Water (U.S. EPA, 2002 Region IX):

Not established.

D. Soil

Red phosphorus will slowly degrade by disproportionating and hydrolysis to phosphine (PH₃) and phosphorus acids in the environment. Phosphine is very reactive and usually undergoes rapid oxidation. The final products, phosphates, are harmless. In wastewater, red phosphorus will adsorb to sewage sludge. Red phosphorus is harmful to aquatic organisms (EFRA, 2001).

Preliminary Remediation Goal for Residential Soil (U.S. EPA, 2002 Region IX): Not established.

E. Air

No information available.

Preliminary Remediation Goal for Ambient Air (U.S. EPA, 2002 Region IX):

Not established.

F. Indoor Surface Contamination

No information available.

X. Personal Protective Equipment

Wear dust-proof goggles, vinyl rubber gloves, protective clothing, rubber boots, and for instances where exposure levels are unknown, wear a full-face, positive-pressure, and air-supplied respirator (HSDB, 2001; NJDH, 2003; Mallinckrodt, 2001). Discard contaminated clothing or shoes (Dastech, 2001). If white phosphorus is present as an impurity in red phosphorus, personal protective equipment that is appropriate for possible exposure to white phosphorus will need to be used (Mallinckrodt, 2001).

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